PRODUCTION AND CHARACTERIZATION OF NANO-RDX

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ABSTRACT

Many techniques have been used in the past to produce nanoscale RDX but all suffer difficulties with process scale-up. The approach used in this study is a mechanical approach as opposed to a chemical one such as recrystallization using supercritical fluids such as CO_2.

1. INTRODUCTION

Past studies have shown that energetic materials in smaller size regimes, such as Class 5 material, have shown superior insensitivity characteristics to larger size materials – particularly to impact stimuli. This can be attributed to the lower number of occlusions and dislocations present in these particles. This concept can be taken one step further with particles in the sub-micron range as the number of defects decrease beyond that in the Class 5 material and overall surface area is increased. Recent, unpublished work has shown a decrease in sensitivity, by a factor of two, to impact using 500 nm RDX. This material was also tested in the small-scale gap test (SSGT) and showed a similar level of improvement. These results show great promise for using nano-RDX and nano-HMX to improve the IM characteristics of high explosive formulations and thus improve survivability for the Soldier.

Nanoenergetic materials will benefit the Soldier through the improvement of Insensitive Munitions without a sacrifice to lethality. Nanoenergetic materials, while not subject to the same imperfections within their crystal structure as Class 1 and Class 5 material, will not react to stimuli so readily. This, in turn, will improve survivability. At the same time, this improvement in crystal structure will ensure that the energy release and output of these materials is not compromised in order to meet IM requirements

2. EXPERIMENTAL APPROACH

Class 5 RDX from Holston Army Ammunition Plant was milled to the sub-micron and nanoscale. The material was placed in a suspension consisting of water, isobutanol as a surfactant, and a dispersant to ensure proper wetting of the surface of the material. This solution optimized the milling process by keeping the material in suspension and through the prevention of agglomeration.

Twenty grams of RDX were processed per batch. The twenty grams were placed in the aforementioned solution to create a slurry with 10% solids loading. The precursor materials were pre-mixed and then placed within the mill. An agitation rate was set and samples of the material were drawn from the process every ten minutes. These samples, and the end product, were then analyzed to determine the capabilities of the process and the value of the nano-sized RDX based on a comparison with standard RDX.

Many of the variables were fixed during this iteration of testing, such as the amount and size of grinding media, the type of dispersant and surfactant, and the solids loading, so the focus of this study was towards milling time and milling speed. The material was milled at 2000 RPM, 2500 RPM, 3000 RPM, and 3500 RPM. Samples were taken at ten-minute intervals and each milling operation was stopped after one hour.

This material was then collected, filtered, and dried in a vacuum oven for later coating and subsequent analysis through impact, friction, ESD, and the small-scale gap test.

3. RESULTS AND DISCUSSION

A number of key attributes of the material were analyzed during this study. The particle size distribution was studied to confirm if milling under this process truly produced nano-RDX fully and consistently. The surface characteristics of material were observed in order to determine what an operation such as this does to such a critical attribute of a crystal given that this will affect future formulations work and sensitivity characteristics. Finally, the purity of the RDX was addressed to observe whether the suspension fluid or grinding media used remained as contaminants with the RDX nanoparticles.

3.1 Particle Size Analysis

When performing the particle size analysis, it was necessary to use light-scattering, microscopic, and x-ray diffraction techniques to estimate what the average size and distribution may be. This approach offsets the

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limitations of individual methods; too many assumptions are set for mechanical methods and too little data points are available for visual analysis.

The particle size of the RDX was analyzed over time in order to correlate processing conditions to both mean particle size and particle size distribution (PSD). Figures 1-3 show AFM images of the material over a processing run at 2000 rpm. Based on these images, the material is rendered down quickly to the submicron level. The feed material was designated as Class 5, and roughly has a mean particle size distribution of 30 microns. The mean at time T = 10 minutes, can be inferred to be approximately 1 micron.

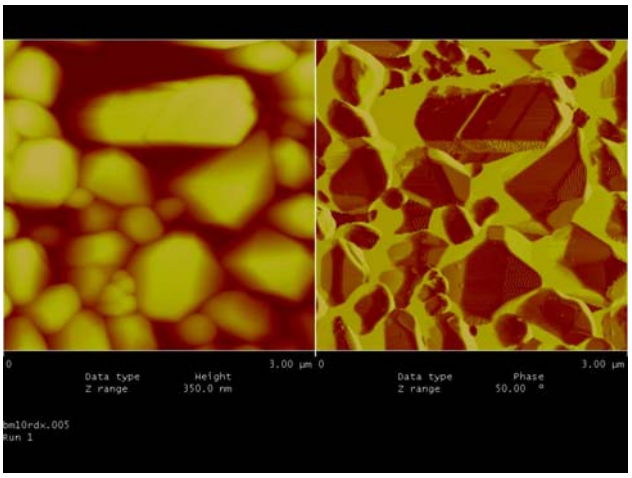

Figure 1: RDX at T=10 min, 2000 RPM

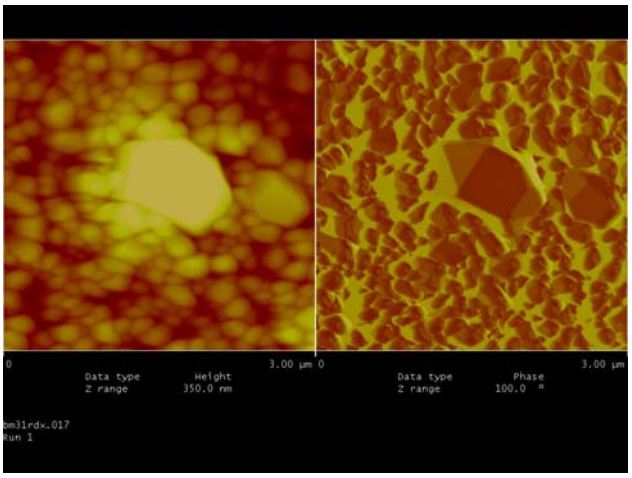

Figure 2: RDX at T=30 min, 2000 rpm

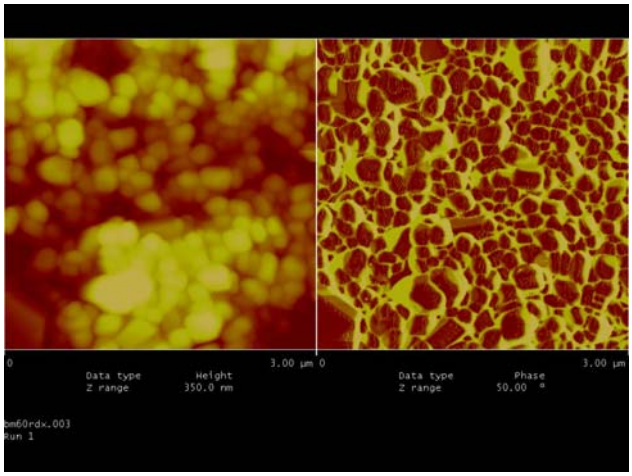

Figure 3: RDX at T=60 min, 2000 rpm

This progression continues during the course of the 60-minute process as observed in Figure 1-3. The images show that the mean particle size continues to decrease but that some larger particles, in the 1+ micron range, continue to persist. Finally, by T=60 minutes, it can be observed that all particles have been reduced below the micron range. Using a Lecotrac particle size analyzer, it was determined that the mean particle size is 310 nm. This progression, and the subsequent distribution of particle size on a cumulative basis, is represented in Figure 4. It must be noted that such a direct correlation was not seen for later experiments. This discrepancy is discussed in Section 3.4, Processing Lessons Learned.

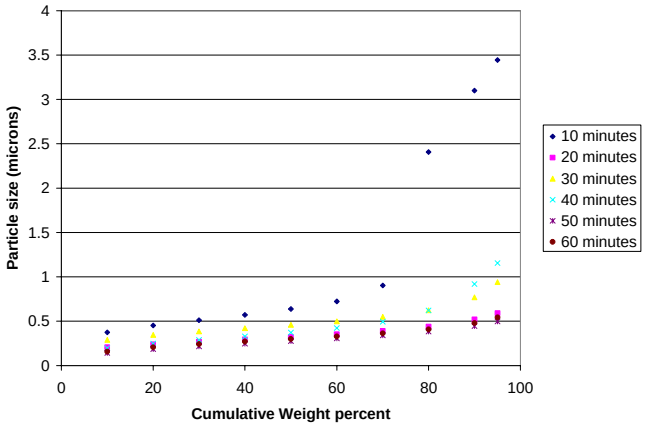

Figure 4: Cumulative Particle Size Distribution Over Time for RDX Milled at 2000 RPM

3.2 Product Purity and Nanostructure

X-ray diffraction (XRD) was used to determine crystallite size and to detect any impurities generated by the milling process. Crystallite size is the measure of the primary crystal size of the individual crystals that make up each particle in this material. This is a determinant of

some of the properties of the material, such as the mechanical strength of the nano-RDX. It was determined that, for example, the average crystallite size for nano-RDX produced from milling the Class 5 RDX at 3000 rpm for 60 minutes was 65 nm to 70 nm. The diffraction spectra, shown in Figure 5, provide no evidence that the milling material adversely affects the purity of the RDX in any way.

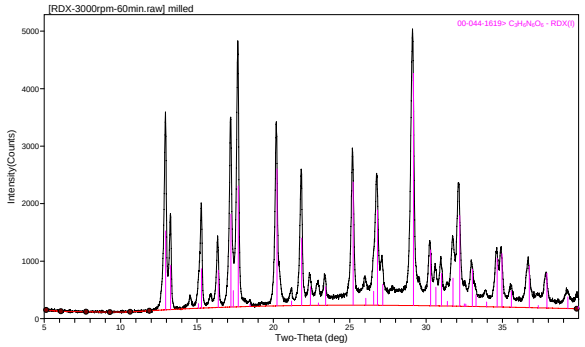

Figure 5: Diffraction Pattern of Milled nano-RDX

The purity of the material was also measured using Micro-Raman FTIR. The threat of contamination was assumed to be high for this type of operation, so these techniques were used to detect both the presence of trace amounts of the grinding media as well as any traces of solvent. The results of the Micro-Raman are shown in Figure 6.

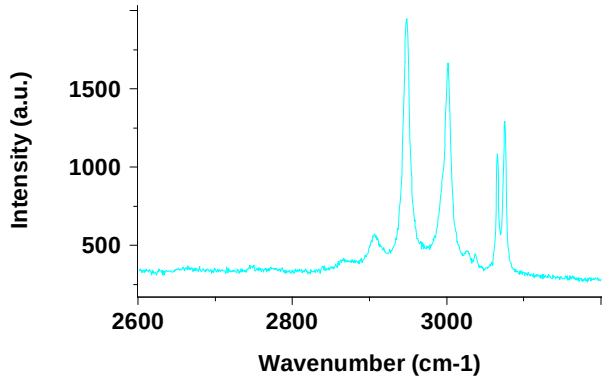

Figure 6: Emissions Spectra for Nano-RDX

The resulting spectra from the Micro-Raman indicate that the material is pure and that no solvent remained on its surface after processing.

The surface characteristics and morphology of the material were also evaluated with the AFM, and additional particle size analysis was performed with a Field Emission Scanning Electron Microscope (FESEM). Both of these instruments provided insight as to the nature of the surface of the material. As can be observed from the AFM pictures, Figures 1-3, and from the FESEM pictures, Figures 7-8, the surfaces of the particles are smooth despite the milling and the distribution is uniform.

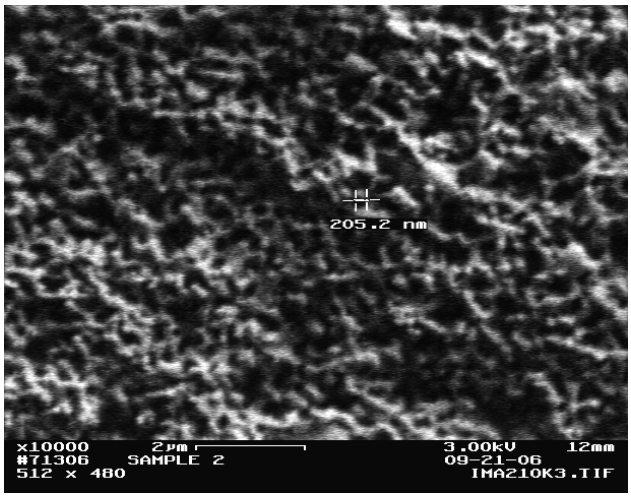

Figure 7: FESEM Image of Milled RDX at 10000x Magnification

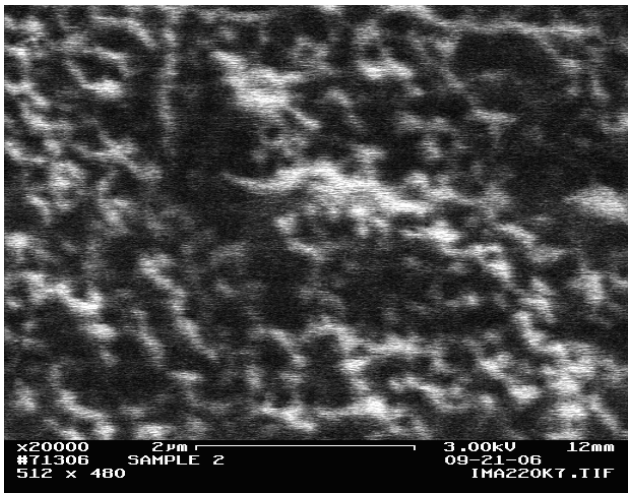

Figure 8: FESEM Image of Milled RDX at 20000x Magnification

3.3 Sensitivity Analysis

The most compelling justification for producing nanoenergetic materials is their potential ability to enhance the survivability of the Warfighter through decreased sensitivity to outside stimuli. A study was performed on the nano-RDX produced with this mechanical method to determine whether it exhibited sensitivity characteristics that were analogous to that of nano-RDX produced by chemical means and, at the least, to prove that its characteristics are superior to that of standard, micron-sized RDX.

The nano-RDX was coated with a wax binder so that its sensitivity could be compared to both nano-RDX produced by supercritical fluids and to micron-sized RDX generated by standard crystallization. Before coating, this material was first tested by differential scanning calorimetry to determine when self-heating occurs. As can be seen in Figure 9, the melting point and thermal onset of this material is similar to that of standard RDX.

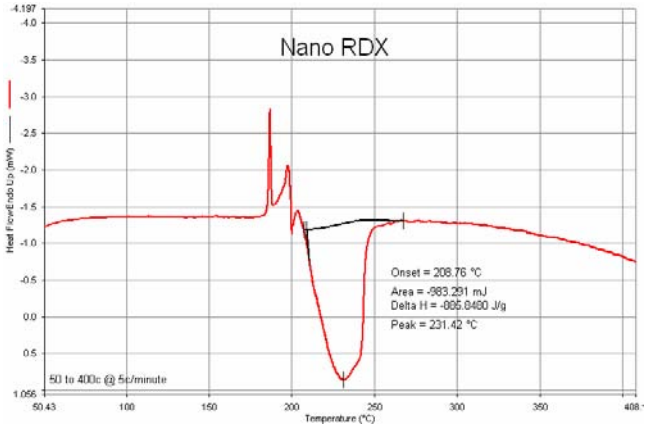

Figure 9: DSC Results for Nano-RDX Produced by Milling Process

The coated material was put through the standard battery of tests such as impact, friction, and electrostatic sensitivity in order to determine its basic sensitivity characteristics. The results are shown in Table 1 below:

	Impact (cm)	Friction (N)	ESD (J)
Milled Nano-RDX	54.1	216	0.25
RESS Nano-RDX	75	216	0.25
Standard RDX	23	216	0.25

Table 1: Sensitivity of Milled Nano-RDX vs. Standard and Nano-RDX produced by the RESS process

There was a significant decrease in sensitivity over impact in comparison with standard, micron-sized RDX but the milled nano-RDX still fell short of nano-RDX produced by the RESS process. However, the milling process is yet to be optimized to produce particle size similar to or smaller than that produced by RESS. Additionally, the milling process is highly scalable and already produces more material than a typical RESS process.

The material was loaded and then tested with the Small Scale Gap Test (SSGT). The SSGT measures the sensitivity of the material to shock. This test was particularly significant, even more so than the tests mentioned above, in that SSGT provides a much greater insight into the nature of the material from an Insensitive Munitions (IM) perspective. Thus, this test shows us how effective the material will be within the context of an end-item used by the Warfighter and how its response would directly affect the safety and survivability of those using it. The results are shown below in Table 2:

	50% pt (dBg)
Milled Nano-RDX	5.9375
Standard RDX	5.075

Table 2: Comparison of Small-Scale Gap Test Data, in deciBangs

The results were extremely encouraging as they show a clear performance improvement, 18% increase, over standard RDX. In the future, it will also be shown that the milled material's performance in the SSGT is equivalent to that of nano-RDX produced by the RESS process. Work that is yet unpublished shows only a 7% increase of RESS-produced nano-RDX beyond that of the milled nano-RDX. The significance of this result is that the benefits for using nano-RDX are known to be strong and this milling operation is a viable way to produce this material at the production level in order to take advantage of these benefits. Even more significant is, despite processing issues addressed below, the material is more easily coated and pressed than RESS nano-RDX, thus indicating an efficacy that has not been demonstrated for nano-RDX at this time despite its potential.

3.4 Processing Lessons Learned

The process to produce nano-RDX by this means is both elegant and simple. Unfortunately, it is not without its limitations. The major issue faced with this particular process is recovery of material. Due to the nature of nanoparticles with their high surface area, they naturally "coat" surfaces that they touch. One additional problem is that they are extremely hard to separate out of solution given the fact that standard filters cannot effectively be used, especially in a situation in which an effective surfactant and dispersant is present.

With initial testing, the material was collected by setting the outlet of the mill over a number of collection containers and allowing the bulk of the material to drain into it. The material was then left in solution to be tested by AFM, FESEM, and particle size analysis. After this testing was complete, the material was then filtered and dried. In order for the material to be filtered effectively, something other than conventional filter paper had to be used. The only item available which fit this capability was the Stericup by Millipore. The Stericup uses filter paper with 100 nm pore size and is mainly used in the biological sciences. It was generally found that 250 mL of solution required a minimum of 30 minutes of filtering

for the bulk of the solvents to be separated from the nano-RDX. Another general requirement to ensure expediency in filtration was the use of more than one filter as the 100 nm pores would clog over time. The results of the Stericup were encouraging, but they are cost-prohibitive in relation to standard filter paper and can generally only be used once.

Two other processing issues, which also affected analysis, were the loss of material within the mill and the loss of material to the surfaces of the storage containers. The initial five runs from which the material was milled at varying speeds and at varying solids loading resulted in an average of 25% yield of material after the full recovery process was accomplished. This was partly due to loss within the mill as only the bulk of the material was collected while the remainder, assumed to be only trace amounts, was cleared from the system with deionized water. A good portion of the material also remained within the crevices of the small, plastic containers that they were stored in. There was no truly effective way of removing this material despite the use of isobutanol, deionized water, and other solvents. Ultimately, these initial five runs yielded only 25 grams of material despite the fact each run processed 20 grams of Class 5 RDX. This was corrected with later experiments as it was determined that minimizing time between each step and filtering the first wash of the mill allowed for much greater recovery. Minding these issues enabled an increase in the yield to 80%. It is believed that these problems will be ameliorated further after discussion with the vendor.

The material's propensity to stick to the walls of plastic containers has also affected the particle size analysis and the material's ability to stay in suspension. With some later runs, the correlation between the Lecotrac and the AFM pictures, as observed in Figures 1-4, was not as evident. It was noted that the particle size obtained by the Lecotrac increased in accordance with the time the material remained in solution within the plastic containers. This resulted in bimodal distributions with one peak in the 300 nm to 400 nm range and a second, larger peak in the 3 micron to 4-micron range. This is an oddity considering the solution contained 5% surfactant and dispersant. In preliminary tests during the selection process of the mill, this same solution was placed into a glass container without incident. The dispersion of the material in these glass containers remains excellent even though they have remained in these containers for two years. More work needs to be done to understand why this more recent phenomena occurred.

Finally, the material demonstrated a drastic change in its properties after allowing it to sit within the filter over the course of two days. The material was extracted from the filter, broken up, and then placed within a solution of isobutanol and water (50/50 by weight) and then sonicated until the material appeared to be in the submicron range based on visual inspection. This material was analyzed using the FESEM with the resulting images shown in Figures 10-12. These images raised more questions than they answered.

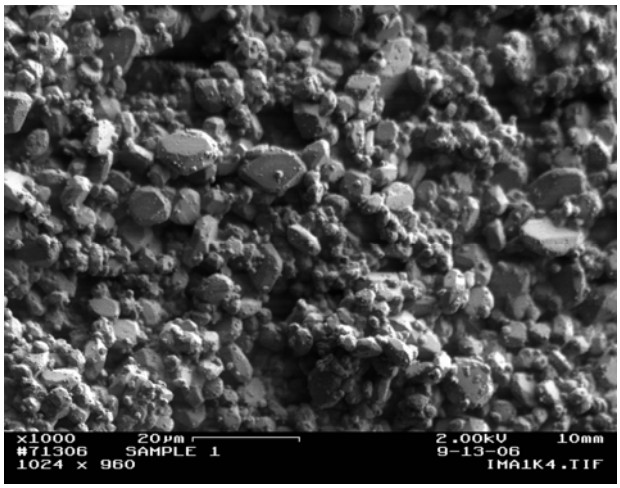

Figure 10: FESEM Image of Milled and Dried RDX at 1000x Magnification

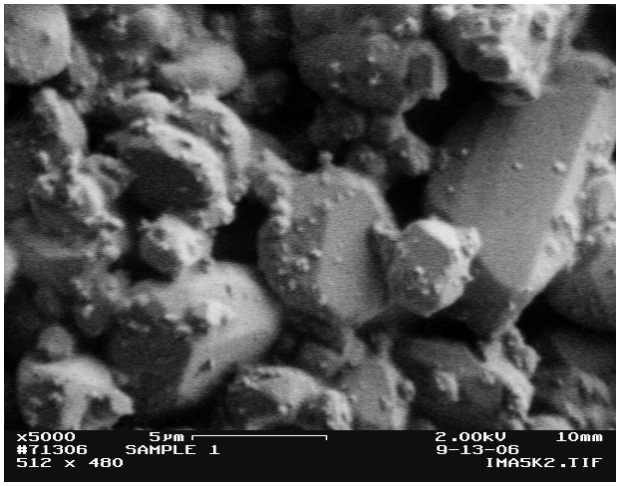

Figure 11: FESEM Image of Milled and Dried RDX at 5000x Magnification

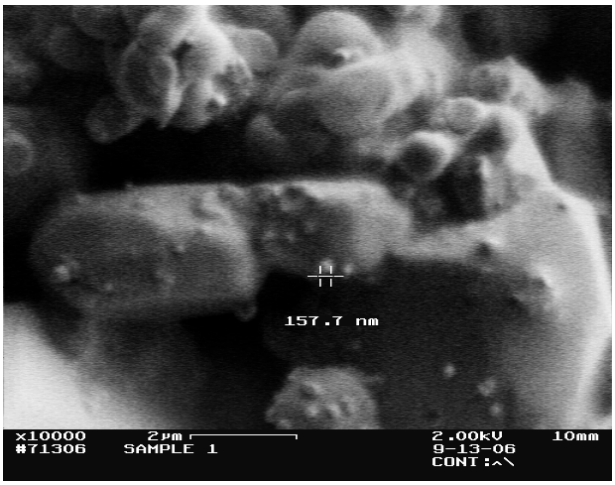

Figure 12: FESEM Image of Milled and Dried RDX at 10000x Magnification

Based on these FESEM images, the nano-RDX reconstituted back into larger, micron-sized particles under the conditions they were exposed to during storage and preparation. The average particle size is estimated to be approximately 5 microns with a number of particles in the 10-micron range or slightly above. Figures 11 and 12 paint a more interesting picture, still. Both images provide 5000x and 10000x magnification respectively so the surfaces of the particles are more well-defined. It is noted that there are a large number of nanoparticles residing on these surfaces and that all of particle shown in the field of view are very smooth and regularly shaped. In Figure 13, it appears that some of these nanoparticles are absorbed into the surface of the larger particles.

More study needs to be conducted to address this problem, but it appears that through exposure to the remaining solvent trapped within the interstices between the particles while drying, and further exposure through sonication within a solvent system with no dispersant present, that the material recrystallized while in solution. This assumption is based on the idea that there is a critical diameter that is required for a particle to remain in equilibrium while in solution in a given solvent system. If it does not reach this critical diameter, then it will go back into solution until a particle that is large enough is formed. This is one of the many theories used for the development of recrystallization processes as it allows one to determine an optimal solvent system for reaching a target size. In this case, it seems very possible that the particles, while in close contact with each other, recrystallized and formed larger particles at their grain boundaries, which cannot be seen here. RDX reacts while under the FESEM so it likely that it is not possible to see the grain boundaries even if they are present.

CONCLUSIONS

This study was an attempt to provide an engineering solution towards solving the problem of producing nanoenergetic materials at larger scales. The obstacles that had to be overcome were many, but were quite manageable. Ultimately, it was proven that nano-RDX produced by mechanical means is almost the equivalent to nano-RDX produced by the RESS process from a sensitivity standpoint. Furthermore, this material is much easier to handle and can already be produced in larger quantities than that which is afforded by the RESS process.

The way forward requires that the process be optimized to maximize yield and a stronger correlation must be drawn between processing conditions and particle size distribution. Understanding the process parameters and the methods of analysis used to evaluate the product will allow one to tailor the output to meet specific end-item needs and will also accelerate the scale-up of the process to production level.